

FORM PTO-1390 (Modified)
(REV 11-2000)

U.S. DEPARTMENT OF COMMERCE PATENT AND TRADEMARK OFFICE

ATTORNEY'S DOCKET NUMBER

70301/56944

TRANSMITTAL LETTER TO THE UNITED STATES

DESIGNATED/ELECTED OFFICE (DO/EO/US)

CONCERNING A FILING UNDER 35 U.S.C. 371

U.S. APPLICATION NO. (IF KNOWN, SEE 37 CFR

10/049969

INTERNATIONAL APPLICATION NO.

PCT/EP00/07317

INTERNATIONAL FILING DATE

July 28, 2000

PRIORITY DATE CLAIMED

August 13, 1999 AND October 19, 1999

TITLE OF INVENTION

COMPOSITION WHICH CURES USING VISIBLE LIGHT AND ITS USE

APPLICANT(S) FOR DO/EO/US

ZIMMERMAN, Michael

LANGE, Rudiger

Applicant herewith submits to the United States Designated/Elected Office (DO/EO/US) the following items and other information:

1. ☒ This is a **FIRST** submission of items concerning a filing under 35 U.S.C. 371.
2. ☐ This is a **SECOND** or **SUBSEQUENT** submission of items concerning a filing under 35 U.S.C. 371.
3. ☒ This is an express request to begin national examination procedures (35 U.S.C. 371(f)). The submission must include items (5), (6), (9) and (24) indicated below.
4. ☐ The US has been elected by the expiration of 19 months from the priority date (Article 31).
5. ☒ A copy of the International Application as filed (35 U.S.C. 371 (c) (2))
 - a. ☐ is attached hereto (required only if not communicated by the International Bureau).
 - b. ☒ has been communicated by the International Bureau.
 - c. ☐ is not required, as the application was filed in the United States Receiving Office (RO/US).
6. ☒ An English language translation of the International Application as filed (35 U.S.C. 371(c)(2)).
 - a. ☒ is attached hereto.
 - b. ☐ has been previously submitted under 35 U.S.C. 154(d)(4).
7. ☐ Amendments to the claims of the International Application under PCT Article 19 (35 U.S.C. 371 (c)(3))
 - a. ☐ are attached hereto (required only if not communicated by the International Bureau).
 - b. ☐ have been communicated by the International Bureau.
 - c. ☐ have not been made; however, the time limit for making such amendments has NOT expired.
 - d. ☐ have not been made and will not be made.
8. ☐ An English language translation of the amendments to the claims under PCT Article 19 (35 U.S.C. 371(c)(3)).
9. ☒ An oath or declaration of the inventor(s) (35 U.S.C. 371 (c)(4)).
10. ☐ An English language translation of the annexes to the International Preliminary Examination Report under PCT Article 36 (35 U.S.C. 371 (c)(5)).
11. ☒ A copy of the International Preliminary Examination Report (PCT/IPEA/409).
12. ☒ A copy of the International Search Report (PCT/ISA/210).

Items 13 to 20 below concern document(s) or information included:

13. ☐ An Information Disclosure Statement under 37 CFR 1.97 and 1.98.
14. ☒ An assignment document for recording. A separate cover sheet in compliance with 37 CFR 3.28 and 3.31 is included.
15. ☒ A **FIRST** preliminary amendment.
16. ☐ A **SECOND** or **SUBSEQUENT** preliminary amendment.
17. ☐ A substitute specification.
18. ☐ A change of power of attorney and/or address letter.
19. ☐ A computer-readable form of the sequence listing in accordance with PCT Rule 13ter.2 and 35 U.S.C. 1.821 - 1.825.
20. ☐ A second copy of the published international application under 35 U.S.C. 154(d)(4).
21. ☐ A second copy of the English language translation of the international application under 35 U.S.C. 154(d)(4).
22. ☒ Certificate of Mailing by Express Mail
23. ☒ Other items or information:

Verification of Translation; WO 01/12679 A1 (1st page); PCT/IB/308; PCT/RO/101

U.S. APPLICATION NO. (IF KNOWN, SEE 37 CFR 1.492(a)(1)-(5)) <div style="font-size: 1.5em; font-weight: bold;">10/049969</div>	INTERNATIONAL APPLICATION NO. <div style="font-weight: bold;">PCT/EP00/07317</div>	ATTORNEY'S DOCKET NUMBER <div style="font-weight: bold;">70301/56944</div>
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24. The following fees are submitted: BASIC NATIONAL FEE (37 CFR 1.492 (a) (1) - (5)) :				CALCULATIONS PTO USE ONLY	
<input type="checkbox"/> Neither international preliminary examination fee (37 CFR 1.482) nor international search fee (37 CFR 1.445(a)(2)) paid to USPTO and International Search Report not prepared by the EPO or JPO \$1040.00					
<input checked="" type="checkbox"/> International preliminary examination fee (37 CFR 1.482) not paid to USPTO but International Search Report prepared by the EPO or JPO \$890.00					
<input type="checkbox"/> International preliminary examination fee (37 CFR 1.482) not paid to USPTO but international search fee (37 CFR 1.445(a)(2)) paid to USPTO \$740.00					
<input type="checkbox"/> International preliminary examination fee (37 CFR 1.482) paid to USPTO but all claims did not satisfy provisions of PCT Article 33(1)-(4) \$710.00					
<input type="checkbox"/> International preliminary examination fee (37 CFR 1.482) paid to USPTO and all claims satisfied provisions of PCT Article 33(1)-(4) \$100.00					
ENTER APPROPRIATE BASIC FEE AMOUNT =				<div style="border: 1px solid black; display: inline-block; padding: 2px 10px;">\$890.00</div>	
Surcharge of \$130.00 for furnishing the oath or declaration later than <input type="checkbox"/> 20 <input type="checkbox"/> 30 months from the earliest claimed priority date (37 CFR 1.492 (e)).				<div style="border: 1px solid black; display: inline-block; padding: 2px 10px;">\$0.00</div>	
CLAIMS	NUMBER FILED	NUMBER EXTRA	RATE		
Total claims	40 - 20 =	20	x \$18.00	<div style="border: 1px solid black; display: inline-block; padding: 2px 10px;">\$360.00</div>	
Independent claims	2 - 3 =	0	x \$84.00	<div style="border: 1px solid black; display: inline-block; padding: 2px 10px;">\$0.00</div>	
Multiple Dependent Claims (check if applicable). <input type="checkbox"/>				<div style="border: 1px solid black; display: inline-block; padding: 2px 10px;">\$0.00</div>	
TOTAL OF ABOVE CALCULATIONS =				<div style="border: 1px solid black; display: inline-block; padding: 2px 10px;">\$1,250.00</div>	
<input type="checkbox"/> Applicant claims small entity status. See 37 CFR 1.27. The fees indicated above are reduced by 1/2.				<div style="border: 1px solid black; display: inline-block; padding: 2px 10px;">\$0.00</div>	
SUBTOTAL =				<div style="border: 1px solid black; display: inline-block; padding: 2px 10px;">\$1,250.00</div>	
Processing fee of \$130.00 for furnishing the English translation later than <input type="checkbox"/> 20 <input type="checkbox"/> 30 months from the earliest claimed priority date (37 CFR 1.492 (f)).				<div style="border: 1px solid black; display: inline-block; padding: 2px 10px;">\$0.00</div>	
TOTAL NATIONAL FEE =				<div style="border: 1px solid black; display: inline-block; padding: 2px 10px;">\$1,250.00</div>	
Fee for recording the enclosed assignment (37 CFR 1.21(h)). The assignment must be accompanied by an appropriate cover sheet (37 CFR 3.28, 3.31) (check if applicable).				<div style="border: 1px solid black; display: inline-block; padding: 2px 10px;">\$40.00</div>	
TOTAL FEES ENCLOSED =				<div style="border: 1px solid black; display: inline-block; padding: 2px 10px;">\$1,290.00</div>	
				Amount to be: refunded \$	
				charged \$	

- a. ☒ A check in the amount of \$1,290.00 to cover the above fees is enclosed.
- b. ☐ Please charge my Deposit Account No. _____ in the amount of _____ to cover the above fees. A duplicate copy of this sheet is enclosed.
- c. ☒ The Commissioner is hereby authorized to charge any additional fees which may be required, or credit any overpayment to Deposit Account No. 04-1105. A duplicate copy of this sheet is enclosed.
- d. ☐ Fees are to be charged to a credit card. **WARNING:** Information on this form may become public. **Credit card information should not be included on this form.** Provide credit card information and authorization on PTO-2038.

NOTE: Where an appropriate time limit under 37 CFR 1.494 or 1.495 has not been met, a petition to revive (37 CFR 1.137(a) or (b)) must be filed and granted to restore the application to pending status.

SEND ALL CORRESPONDENCE TO:

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SIGNATURE

George W. Neuner

NAME

26,964

REGISTRATION NUMBER

DATE

Attorney Docket No. 70301.56944

IN THE UNITED STATES PATENT AND TRADEMARK OFFICE

APPLICANT: ZIMMERMAN, Michael
LANGE, Rüdiger

SERIAL NO. N/A

FILED: Herewith

FOR: COMPOSITION WHICH CURES USING VISIBLE
LIGHT AND ITS USE

BOX PATENT APPLICATION
COMMISSIONER FOR PATENTS
WASHINGTON, DC 20231

Sir:

PRELIMINARY AMENDMENT

Please amend the application as follows.

In the Claims:

Please cancel claims 1-22 and enter the following new claims.

--23. A method for producing a three-dimensional object by sequential selective solidification of layers of the composition at positions corresponding to the cross-section of the object, the method comprising irradiating in each layer of a composition comprising the following constituents:

- (a) 2-99 wt.% of at least one compound comprising a group selected from an acrylate group, a methacrylate group, a vinyl group, an

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epoxy group, an oxetane group, an acryl-epoxy oligomer group or a methacryl-epoxy oligomer group, or at least one resin composition comprising at least one polymerisable polysiloxane,

- (b) 0.01-7 wt.% of at least one initiator,
- (c) 0-5 wt.% of at least one co-initiator, and
- (d) 0-85 wt.% of one or more modifiers selected from the group consisting of fillers, dyestuffs, pigments, flow improvers, thixotropic agents, polymeric thickeners, oxidising additives, stabilisers and retardants.

24. The method according to claim 23, further comprising producing models, individually manufactured single products or mass-produced sales products.

25. The method according to claim 23, wherein constituent (a) comprises an ormocer.

26. The method according to claim 23, wherein constituent (a) is a resin composition comprising polymerisable polysiloxanes, which can be hardened photochemically or thermally, in the presence of initiators or one which is self-hardening, which can be obtained by hydrolytic condensation of one or more hydrolytically condensable compounds of silicon, wherein 1 to 100 mole %, based on the monomeric compounds, are selected from

- (i) silanes of the general formula (I),



wherein the radicals X, Y and R are the same or different and have the following meaning:

R = alkyl, alkenyl, aryl, alkylaryl or arylalkyl

X = hydrogen, halogen, hydroxyl, alkoxy, acyloxy, alkylcarbonyl, alkoxy carbonyl, or NR'₂

where R' = hydrogen, alkyl or aryl,

Y = a substituent, which comprises a substituted or unsubstituted 1,4,6-trioxyspiro-[4,4]-nonane radical,

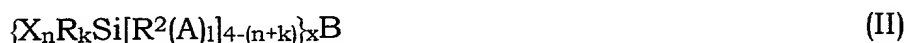
n=1, 2 or 3,

m=1, 2 or 3,

where n+m ≤ 4,

and/or from

(ii) silanes of the general formula (II),



wherein the radicals A, R, R² and X are the same or different, where all variables have the same meaning as defined above, and

A = O, S, PR', POR', NHC(O)O or NHC(O)NR',

B = straight-chain or branched organic radical, which is derived from a compound B' having at least one (for l = 1 and A = NHC(O)O or NHC(O)NR') or at least two C=C double bonds and 5 to 50 carbon atoms, where R' = hydrogen, alkyl or aryl,

R² = alkylene, arylene or alkylene-arylene,

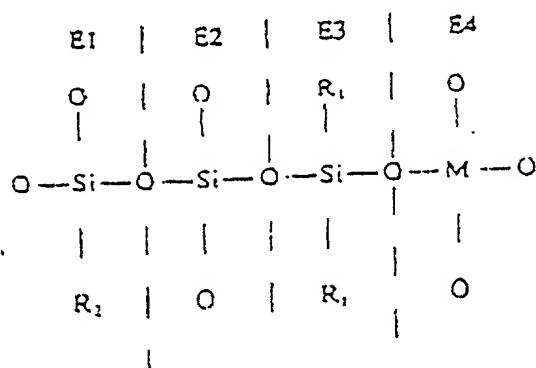
k = 0, 1 or 2,

l = 0 or 1, and

x = a whole number, the maximum value of which corresponds to the number of double bonds in the compound B' minus 1, or is equal to the number of double bonds in the compound B', when l = 1 and A represents NHC(O) or NHC(O)NR'.

27. The method according to claim 30, wherein the polymerisable polysiloxane further comprises a hydrolytically condensable compound of an element selected from the group consisting of B, Ba, Ti, Zr, Al, Sn, the transition metals, the lanthanides and the actinides, or a pre-condensate derived from the above-mentioned compounds.

28. the method according to claim 23, wherein constituent (a) is a resin composition comprising a compound composed of the structural element E 2 and at least one of the structural elements E 1, E 3 or E 4 of the general formula



wherein:

R₁ denotes a methyl, ethyl, n-propyl, isopropyl or an optionally CH₃-C₃H₇-substituted phenyl radical,

R₂ denotes a CH₂=CH, CH₂=CHCOO(CH₂)_n or CH=C(CH₃)-COO(CH₂)_n radical, or R₁,

n denotes 0, 1, 2 or 3, and

M denotes titanium or zirconium.

29. The method according to claim 23, wherein constituent (a) is present in a quantity of 10-95 wt. %.

30. The method according to claim 23, further comprising hardening the composition using a wavelength range from 350-700 nm.

31. The method according to claim 23, wherein constituent (a) comprises a component selected from the group consisting of aliphatic diurethane methacrylate, tetraethoxylated bisphenol A dimethacrylate, aliphatic urethane methacrylate, 2-hydroxyethyl acrylate, hydroxypropyl acrylate, methyl methacrylate, ethyl methacrylate, n-propyl methacrylate, isopropyl methacrylate, butyl methacrylate, 2-ethylhexyl methacrylate, methacrylic acid esters, isobornyl methacrylate, benzyl methacrylate, cyclohexyl methacrylate, n-hexyl methacrylate, ethyl triglycol methacrylate, tetrahydrofurfuryl methacrylate, hydroxyalkyl methacrylates, 2-hydroxyethyl methacrylate, alkoxyethyl methacrylate, allyl methacrylate, ethylene glycol dimethacrylate, diethyl glycol dimethacrylate, triethylene glycol dimethacrylate, tetraethylene glycol dimethacrylate, polyethylene glycol dimethacrylates, 1,3-butane diol dimethacrylate, 1,4-butane diol dimethacrylate, 1,6-hexane diol dimethacrylate, 1,12-dodecane diol dimethacrylate, glycerin-1,3-dimethacrylate, diurethane dimethacrylate, trimethylol propane trimethylacrylate, 1,3,5,7-tetrakis-(2,1-ethanediyl-3,4-epoxycyclohexyl)-1,3,5,7-tetramethylcyclotetrasiloxane, 1,10-decanediyl-bis(oxymethylene)-bis(3-ethyloxetane), 1,3,5,7,9-pentakis-3,5,7,9-pentamethylcyclopentasiloxane, vinylcyclohexene oxide, vinylcyclohexene dioxide, 3,4-epoxy-6-methylcyclohexylmethyl-3,4-epoxy-6-methylcyclohexane carboxylate, bis(2,3-epoxycyclopentyl)ether; 3,4-epoxy-6-methylcyclohexylmethyl adipate, 3,4-epoxycyclohexyl-15,5-spiro-3,4-epoxy(cyclohexane-metadioxane), 1,4-butanediyl-bis(oxymethylene)-bis(3-ethyloxetane), 3,4-epoxycyclohexylmethyl-3,4-epoxycyclohexane carboxylate, 1,1,3,3-tetramethyl-1,3-bis(2,1-ethanediyl-3,4-epoxycyclohexyl)disiloxane, bis-(3,4-epoxycyclohexylmethyl) adipate, monovinyl ether, divinyl ether, hydroxyvinyl ether, aminovinyl ether, trivinyl

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ether, triethylene glycol divinyl ether, 4-hydroxybutylvinyl ether, propenyl ether from propylene carbonate, dodecyl-vinyl ether, triethylene glycol divinyl ether, alkyl-vinyl ether, ethylene glycol-monovinyl ether, diethylene glycol divinyl ether, butane diol-monovinyl ether, butane diol-divinyl ether, hexane diol-divinyl ether, ethylene glycol-butyl-vinyl ether, cyclohexane-dimethanol-monovinyl ether and cyclohexane-dimethanol-divinyl ether, 2-ethyl-hexyl-vinyl ether, poly-THF-divinyl ether, cyclohexyl-vinyl ether, tert.-butyl-vinyl ether, tert.-amyl-vinyl ether, ethylene glycol-divinyl ether, diethylene glycol-monovinyl ether, hexane diol-monovinyl ether, tetraethylene glycol-divinyl ether, trimethylol-propane-trivinyl ether, aminopropylvinyl ether and 2-diethylaminoethyl-vinyl ether.

32. The method according to claim 23, wherein constituent (b) comprises:

for free-radical hardening, a component selected from the group consisting of phosphine oxides, benzoin ethers, benzil ketals, acetophenones, benzophenones, thioxanthenes, α -dicarbonyl compounds, bisimidazoles, metallocenes, aryl-tert.-butyl peresters and fluorones, or

for cationic hardening, a component selected from the group consisting of aryl diazonium salts, aryl sulphonium salts, aryl iodonium salts, ferrocenium salts and phenylphosphonium-benzophenone salts, or a mixture thereof.

33. The method according to claim 32, wherein constituent (b) comprises a component selected from the group consisting of diphenyl-2,4,6-trimethylbenzoylphosphine oxide, benzoin, benzoin-alkyl ether, benzildialkyl ketals, α -hydroxyacetophenone, dialkoxyacetophenone, α -aminoacetophenone, i-propylthioxanthone, camphor-quinone, titanocene, ferrocene, and 5,7-diiodo-3-butoxy-6-fluorone.

34. The method according to claim 23, wherein constituent (c) comprises:

for free-radical hardening, a component is selected from the group consisting of tertiary amines, diaryl iodonium compounds, borates, organic phosphites and thioxanthenes,

for cationic hardening, a component is selected from the group consisting of xanthenes, fluorenes, fluorones and/or α -dicarbonyl compound, or a mixture thereof.

35. The method according to claim 34, wherein constituent (c) comprises a component selected from the group consisting of N,N-dimethyl-p-toluidine, N,N-dihydroxyethyl-p-toluidine, and N,N-dialkyl-alkylaniline, butyrylcholine-triphenylbutyl borate.

36. The method according to claim 23, wherein constituent (d) comprises an anthraquinone dyestuff.

37. The method according to claim 23, wherein constituent (d) comprises a filler selected from the group consisting of silicon dioxide, pyrogenic silicon dioxide, amorphous silicic acid, aluminium oxide, ceramic, quartz, ground glass, fragment polymer, silica gel, minerals, fibres and fabrics.

38. The method according to claim 37, wherein constituent (d) comprises a fibre selected from the group consisting of glass fibres, carbon fibres, textile fibres and metal fibres, which is present individually or in the form of a tape, mat, hose or cord, or in the form of a bundle of continuous fibres.

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39. The method according to claim 23, wherein constituent (d) comprises a silanised filler.

40. The method according to claim 23, wherein constituent (d) comprises hydroquinone, hydroquinone monomethyl ether, pyrocatechol, 2,6-di-tert.-butyl-4-methylphenol.

41. The object produced by the method according to claim 23.

42. A process for producing a tooth filling by sequential layered solidification of a composition at positions corresponding to the cross-section of the filling in the particular layer, the process comprising solidifying in each layer a composition comprising the following constituents:

- (a) 2-99 wt.% of at least one compound comprising a group selected from an acrylate group, a methacrylate group, a vinyl group, an epoxy group, an oxetane group, an acryl-epoxy oligomer group or a methacryl-epoxy oligomer group, or at least one resin composition comprising at least one polymerisable polysiloxane,
- (b) 0.01-7 wt.% of at least one initiator,
- (c) 0-5 wt.% of at least one co-initiator, and
- (d) 0-85 wt.% of one or more modifiers selected from the group consisting of fillers, dyestuffs, pigments, flow improvers, thixotropic agents, polymeric thickeners, oxidising additives, stabilisers and retardants.

43. The process according to claim 42, further comprising the steps of:

- a) producing a computer model of the filling to be produced,
- b) dividing the computer model into layers, which correspond in each case to a cross-section of the filling, and

c) layered curing of the composition at positions corresponding to the cross-section of the filling under the action of visible light.

44. The process according to claim 42, wherein the composition is a paste-like material.

45. The process according to claim 43, wherein the composition is a paste-like material.

46. The process according to claim 42, wherein constituent (a) comprises an ormocer.

47. The process according to claim 42, wherein constituent (a) is a resin composition comprising polymerisable polysiloxanes, which can be hardened photochemically or thermally, in the presence of initiators or one which is self-hardening, which can be obtained by hydrolytic condensation of one or more hydrolytically condensable compounds of silicon, wherein 1 to 100 mole %, based on the monomeric compounds, are selected from

(i) silanes of the general formula (I),



wherein the radicals X, Y and R are the same or different and have the following meaning:

R = alkyl, alkenyl, aryl, alkylaryl or arylalkyl

X = hydrogen, halogen, hydroxyl, alkoxy, acyloxy, alkylcarbonyl, alkoxycarbonyl, or NR'₂

where R' = hydrogen, alkyl or aryl,

Y = a substituent, which comprises a substituted or unsubstituted 1,4,6-trioxyaspiro-[4,4]-nonane radical,

n=1, 2 or 3,

m=1, 2 or 3,

where $n+m \leq 4$,

and/or from

(ii) silanes of the general formula (II),



wherein the radicals A, R, R² and X are the same or different, where all variables have the same meaning as defined above, and

A = O, S, PR', POR', NHC(O)O or NHC(O)NR',

B = straight-chain or branched organic radical, which is derived from a compound B' having at least one (for l = 1 and A = NHC(O)O or NHC(O)NR') or at least two C=C double bonds and 5 to 50 carbon atoms, where R' = hydrogen, alkyl or aryl,

R² = alkylene, arylene or alkylene-arylene,

k = 0, 1 or 2,

l = 0 or 1, and

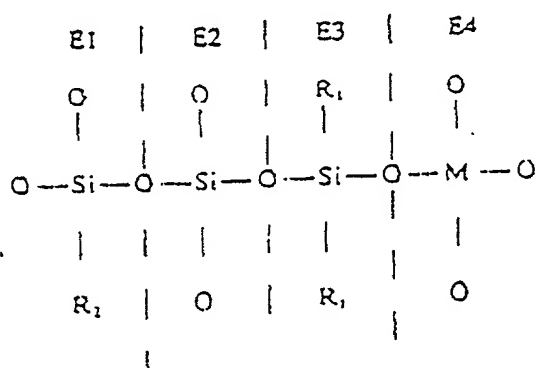
x = a whole number, the maximum value of which corresponds to the number of double bonds in the compound B' minus 1, or is equal to the number of double bonds in the compound B', when l = 1 and A represents NHC(O) or NHC(O)NR'.

48. The process according to claim 47, wherein the polymerisable polysiloxane further comprises a hydrolytically condensable compound of an element selected from the group consisting of B, Ba, Ti, Zr, Al, Sn, the

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transition metals, the lanthanides and the actinides, or a pre-condensate derived from the above-mentioned compounds.

49. The process according to claim 42, wherein constituent (a) is a resin composition comprising a compound composed of the structural element E 2 and at least one of the structural elements E 1, E 3 or E 4 of the general formula



wherein:

R₁ denotes a methyl, ethyl, n-propyl, isopropyl or an optionally CH₃-C₃H₇-substituted phenyl radical,

R₂ denotes a CH₂=CH, CH₂=CHCOO(CH₂)_n or CH=C(CH₃)-COO(CH₂)_n radical, or R₁,

n denotes 0, 1, 2 or 3, and

M denotes titanium or zirconium.

50. The process according to claim 42, wherein constituent (a) is present in a quantity of 10-95 wt. %.

51. The process according to claim 42, further comprising hardening the composition using a wavelength range from 350-700 nm.

52. The process according to claim 42, wherein constituent (a) comprises a component selected from the group consisting of aliphatic diurethane methacrylate, tetraethoxylated bisphenol A dimethacrylate, aliphatic urethane methacrylate, 2-hydroxyethyl acrylate, hydroxypropyl acrylate, methyl methacrylate, ethyl methacrylate, n-propyl methacrylate, isopropyl methacrylate, butyl methacrylate, 2-ethylhexyl methacrylate, methacrylic acid esters, isobornyl methacrylate, benzyl methacrylate, cyclohexyl methacrylate, n-hexyl methacrylate, ethyl triglycol methacrylate, tetrahydrofurfuryl methacrylate, hydroxyalkyl methacrylates, 2-hydroxyethyl methacrylate, alkoxyethyl methacrylate, allyl methacrylate, ethylene glycol dimethacrylate, diethyl glycol dimethacrylate, triethylene glycol dimethacrylate, tetraethylene glycol dimethacrylate, polyethylene glycol dimethacrylates, 1,3-butane diol dimethacrylate, 1,4-butane diol dimethacrylate, 1,6-hexane diol dimethacrylate, 1,12-dodecane diol dimethacrylate, glycerin-1,3-dimethacrylate, diurethane dimethacrylate, trimethylol propane trimethylacrylate, 1,3,5,7-tetrakis-(2,1-ethanediyl-3,4-epoxycyclohexyl)-1,3,5,7-tetramethylcyclotetrasiloxane, 1,10-decanediyl-bis(oxymethylene)-bis(3-ethyloxetane), 1,3,5,7,9-pentakis-3,5,7,9-pentamethylcyclopentasiloxane, vinylcyclohexene oxide, vinylcyclohexene dioxide, 3,4-epoxy-6-methylcyclohexylmethyl-3,4-epoxy-6-methylcyclohexane carboxylate, bis(2,3-epoxycyclopentyl)ether; 3,4-epoxy-6-methylcyclohexylmethyl adipate, 3,4-epoxycyclohexyl-15,5-spiro-3,4-epoxy(cyclohexane-metadioxane), 1,4-butanediyl-bis(oxymethylene)-bis(3-ethyloxetane), 3,4-epoxycyclohexylmethyl-3,4-epoxycyclohexane carboxylate, 1,1,3,3-tetramethyl-1,3-bis(2,1-ethanediyl-3,4-epoxycyclohexyl)disiloxane, bis-(3,4-epoxycyclohexylmethyl) adipate, monovinyl ether, divinyl ether, hydroxyvinyl ether, aminovinyl ether, trivinyl ether, triethylene glycol divinyl ether, 4-hydroxybutylvinyl ether, propenyl ether from propylene carbonate, dodecyl-vinyl ether, triethylene glycol divinyl ether, alkyl-vinyl ether, ethylene glycol-monovinyl ether, diethylene glycol divinyl

ether, butane diol-monovinyl ether, butane diol-divinyl ether, hexane diol-divinyl ether, ethylene glycol-butyl-vinyl ether, cyclohexane-dimethanol-monovinyl ether and cyclohexane-dimethanol-divinyl ether, 2-ethyl-hexyl-vinyl ether, poly-THF-divinyl ether, cyclohexyl-vinyl ether, tert.-butyl-vinyl ether, tert.-amyl-vinyl ether, ethylene glycol-divinyl ether, diethylene glycol-monovinyl ether, hexane diol-monovinyl ether, tetraethylene glycol-divinyl ether, trimethylol-propane-trivinyl ether, aminopropylvinyl ether and 2-diethylaminoethyl-vinyl ether.

53. The process according to claim 42, wherein constituent (b) comprises

for free-radical hardening, a component selected from the group consisting of phosphine oxides, benzoin ethers, benzil ketals, acetophenones, benzophenones, thioxanthenes, α -dicarbonyl compounds, bisimidazoles, metallocenes, aryl-tert.-butyl peresters and fluorones, or

for cationic hardening, a component selected from the group consisting of aryl diazonium salts, aryl sulphonium salts, aryl iodonium salts, ferrocenium salts and phenylphosphonium-benzophenone salts, or a mixture thereof.

54. The process according to claim 53, wherein constituent (b) comprises a component selected from the group consisting of diphenyl-2,4,6-trimethylbenzoylphosphine oxide, benzoin, benzoin-alkyl ether, benzildialkyl ketals, α -hydroxyacetophenone, dialkoxyacetophenone, α -aminoacetophenone, i-propylthioxanthone, camphor-quinone, titanocene, ferrocene, and 5,7-diiodo-3-butoxy-6-fluorone.

55. The process according to claim 42, wherein constituent (c) comprises:

for free-radical hardening, a component is selected from the group consisting of tertiary amines, diaryl iodonium compounds, borates, organic phosphites and thioxanthenes,

for cationic hardening, a component is selected from the group consisting of xanthenes, fluorenes, fluorones and/or α -dicarbonyl compound, or a mixture thereof.

56. The process according to claim 55, wherein constituent (c) comprises a component is selected from the group consisting of N,N-dimethyl-p-toluidine, N,N-dihydroxyethyl-p-toluidine, and N,N-dialkyl-alkylaniline, butyrylcholine-triphenylbutyl borate.

57. The process according to claim 42, wherein constituent (d) comprises an anthraquinone dyestuff.

58. The process according to claim 42, wherein constituent (d) comprises a filler selected from the group consisting of silicon dioxide, pyrogenic silicon dioxide, amorphous silicic acid, aluminium oxide, ceramic, quartz, ground glass, fragment polymer, silica gel, minerals, fibres and fabrics.

59. The process according to claim 58, wherein constituent (d) comprises a fibre selected from the group consisting of glass fibres, carbon fibres, textile fibres and metal fibres, which is present individually or in the form of a tape, mat, hose or cord, or in the form of a bundle of continuous fibres.

60. The process according to claim 42, wherein constituent (d) comprises a silanised filler.

61. The process according to claim 42, wherein constituent (d) comprises hydroquinone, hydroquinone monomethyl ether, pyrocatechol, 2,6-di-tert.-butyl-4-methylphenol.

62. The object produced by process according to claim 42.--

REMARKS

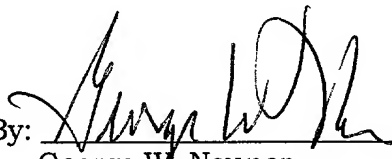
An early examination and notice of allowance are earnestly solicited. Should the Examiner wish to discuss the application, the undersigned attorney would appreciate the opportunity to do so.

Respectfully submitted,

Date:

13 Feb '02

By:


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Composition which cures using visible light and its use

The invention relates to a composition which cures using visible light and its use in a shaping process.

Plastics which cure using visible light are known from European application 0 897 710 for use in dental products.

In addition, it is known to use plastics which cure using UV light in the shaping process of stereolithography.

The object of the invention is to indicate an improved plastic which cures in visible light and which is suitable particularly for shaping processes, such as microphotosolidification, for other rapid-prototyping processes, such as stereolithography or for the production of dental products.

This object is achieved by a composition according to claim 1, a use of the composition according to one of claims 17 to 20, a process according to one of claims 21 to 24 or an object according to claim 25.

Further developments of the invention are indicated in the sub-claims.

Further features and advantages can be seen from the following description of exemplary embodiments of the invention using the figure.

Figure 1 shows a device for the process of producing a three-dimensional object by means of microphotosolidification from a plastic of the invention which cures under the action of visible light.

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Below, the composition of the invention is illustrated using an exemplary embodiment of its use, namely of the production of a three-dimensional object by means of microphotosolidification.

As can be seen from Figure 1, the device has a container 1, which is open at its upper side, having an upper rim 2. A carrier 3 for supporting an object 4 to be formed having an essentially flat and horizontally aligned building platform 5, which may be displaced up and down and positioned in the container 1 by means of a height-adjustment device, is arranged in the container. The entire container 1 is filled up to a level below the upper rim 2 with the composition of the invention in the form of a liquid plastic 6 which cures in visible light. A flat transparent plate 7 made from a material which is transparent to visible light is provided at a predetermined distance below the upper rim 2 of the container 1, such that it is immersed by a predetermined amount into the liquid plastic 6 while the container 1 is filled with the liquid plastic 6.

An illuminating device 8 having a light source 9, such as a halogen, deuterium, plasma, mercury-vapour lamp or a laser, is provided above the container 1 for producing visible light in a wavelength range of, for example 350 to 700 nm. The illuminating device 8 also has a projection optical system and a mask-producing device and a mask 10 for the selective illumination of a particular layer of the three-dimensional object 4 to be formed in a corresponding cross-section. A diaphragm 11 which can be pivoted into the ray path is provided between the illuminating device 8 and the container 1. Furthermore, a control 12 is provided, which is designed so that it controls the diaphragm 11, the mask-producing device 10 and the height-adjustment device of the carrier 3 or the building platform as a function of predetermined object data.

In the process for producing the three-dimensional object 4, the container 1 is filled with the liquid plastic 6 which cures using visible light, and the building platform 5 is displaced by the associated height-adjustment device such that a layer of liquid plastic 6

which cures using visible light in a predetermined layer thickness is formed between the upper side of the building platform 5 and the lower side of the transparent plate 7. Illumination of the plastic layer then takes place in a cross-section corresponding to the three-dimensional object 4 to be formed. The building platform 5 is then displaced vertically downwards in order to form the next layer of liquid light-curable plastic 6 between the upper surface of the object 4 and the transparent plate 7. These steps are repeated successively until the object 4 with its entire height is formed. The mask-producing device 10 is thus actuated via control 12 such that illumination takes place at a light intensity which suffices to penetrate the layer of liquid plastic 6 between the upper surface of the object 4 and the transparent plate 7 and to join it with the underlying already solidified layer of the object 4.

The plastic 6 consists of a composition which cures using or in visible light having

- (a) 2-99 wt.% of at least one compound which contains acrylate and/or methacrylate groups, and/or vinyl and/or epoxy and/or oxetane groups and/or acryl-epoxy oligomer groups and/or methacryl-epoxy oligomer groups, and/or at least one resin composition based on polymerisable polysiloxanes, in particular ormocers,
- (b) 0.01-7 wt.% of at least one initiator,
- (c) 0-5 wt.% of at least one co-initiator,
- (d) 0-85 wt.% of modifiers, such as fillers, dyestuffs, pigments, flow improvers, thixotropic agents, polymeric thickeners, oxidising additives, stabilisers and retardants.

The compound or the compounds of constituent (a) of the composition, which contain acrylate and/or methacrylate groups, cure in visible light by free-radical polymerisation. The following crosslinkable and non-crosslinkable monomers are particularly suitable: aliphatic diurethane methacrylate, tetra-ethoxylated bisphenol A dimethacrylate, aliphatic urethane methacrylate, 2-hydroxyethyl acetate, hydroxypropyl acrylate, methyl methacrylate, ethyl methacrylate, n-propyl methacrylate, iso-propyl methacrylate, butyl methacrylate, 2-ethylhexyl methacrylate, methacrylic acid esters having an ester group of

1 to 13 C atoms, isobornyl methacrylate, benzyl methacrylate, cyclohexyl methacrylate, n-hexyl methacrylate, ethyl triglycol methacrylate, tetrahydrofurfuryl methacrylate, hydroxyalkyl methacrylates having an alkyl group of 1 to 4 C atoms, such as for example 2-hydroxyethyl methacrylate, alkoxyethyl methacrylate having an alkoxy group of 1 to 4 C atoms, allyl methacrylate, ethylene glycol dimethacrylate, diethyl glycol dimethacrylate, triethylene glycol dimethacrylate, tetraethylene glycol dimethacrylate, polyethylene glycol dimethacrylates, 1,3-butane diol dimethacrylate, 1,4-butane diol dimethacrylate, 1,6-hexane diol dimethacrylate, 1,12-dodecane diol dimethacrylate, glycerin-1,3-dimethacrylate, diurethane dimethacrylate, trimethylol propane trimethylacrylate.

The compound or compounds of constituent (a) containing epoxy and/or an oxetane groups cure under the action of visible light by cationic polymerisation. Examples of these are aliphatic or aromatic epoxides, cycloaliphatic epoxides or oxetanes, such as 1,3,5,7-tetrakis-(2,1-ethanediyl-3,4-epoxycyclohexyl)-1,3,5,7-tetramethylcyclotetrasiloxane, 1,10-decanediylbis(oxymethylene)bis(3-ethyloxetane), 1,3,5,7,9-pentakis(2,1-ethanediyl-3,4-epoxycyclohexyl)-1,3,5,7,9-pentamethylcyclopentasiloxane, vinylcyclohexene oxide, vinylcyclohexene dioxide, 3,4-epoxy-6-methylcyclohexylmethyl-3,4-epoxy-6-methylcyclohexane carboxylate, bis(2,3-epoxycyclopentyl)ether; 3,4-epoxy-6-methylcyclohexylmethyl adipate, 3,4-epoxycyclohexyl-5,5-spiro-3,4-epoxy(cyclohexane-metadioxane), 1,4-butane-diylbis(oxymethylene) bis (3-ethyloxetane), 3,4-epoxycyclohexylmethyl-3,4-epoxycyclohexane carboxylate, 1,1,3,3-tetramethyl-1,3-bis(2,1-ethanediyl-3,4-epoxycyclohexyl)disiloxane and/or bis-(3,4-epoxycyclohexylmethyl) adipate, 3,4-epoxycyclohexylmethyl-3'-4'-epoxycyclohexane carboxylate.

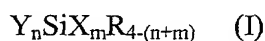
The compound or compounds of constituent (a) of the composition containing vinyl groups, such as for example monovinyl ether, divinyl ether, hydroxyvinyl ether, aminovinyl ether, trivinyl ether, cure by light in free-radical and cationic manner (mostly

cationic). Examples of these are triethylene glycol divinyl ether, 4-hydroxybutylvinyl ether, propenyl ether from propylene carbonate, dodecyl-vinyl ether, triethylene glycol divinyl ether, alkyl-vinyl ether having an alkyl group of 2 to 18 C atoms, ethylene glycol-monovinyl ether, diethylene glycol divinyl ether, butane diol-monovinyl ether, butane diol-divinyl ether, hexane diol-divinyl ether, ethylene glycol-butyl-vinyl ether, cyclohexane-dimethanol-monovinyl ether and cyclohexane-dimethanol-divinyl ether, 2-ethyl-hexyl-vinyl ether, poly-THF-divinyl ether, cyclohexyl-vinyl ether, tert.-butyl-vinyl ether, tert.-amyl-vinyl ether, ethylene glycol-divinyl ether, diethylene glycol-monovinyl ether, hexane diol-monovinyl ether, tetraethylene glycol-divinyl ether, trimethylol-propane-trivinyl ether, aminopropylvinyl ether, 2-diethylaminoethyl-vinyl ether.

The compound or compounds of constituent (a), which contains or contain acryl-epoxy oligomer groups and/or methacryl-epoxy oligomer groups, polymerise under the action of visible light both cationically and by free-radical in the form of so-called dual hardening. The combination of one or more of the above-mentioned cationically polymerising compounds with one or more of the above-mentioned free-radical polymerising compounds likewise leads to dual hardening.

The resin composition or resin compositions based on polymerisable polysiloxanes, in particular ormocers, contains or contain, for example compounds as described in the patents German Patentschrift 4 133 494 or German Offenlegungsschrift 3 903 407. It is for example a resin composition based on polymerisable polysiloxanes which can be hardened photochemically or thermally in the presence of initiators or one which is self-hardening, which can be obtained by hydrolytic condensation of one or more hydrolytically condensable compounds of silicon and optionally other elements from the group B, Ba, Ti, Zr, Al, Sn, the transition metals, the lanthanides and the actinides, and/or pre-condensates derived from the above-mentioned compounds, optionally in the presence of a catalyst and/or a solvent, by the action of water or moisture, wherein 1 to

100 mole %, based on the monomeric compounds, are selected from silanes of the general formula (I),



in which the radicals X, Y and R are the same or different and have the following meaning:

R = alkyl, alkenyl, aryl, alkylaryl or arylalkyl

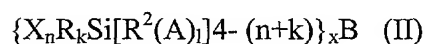
X = hydrogen, halogen, hydroxyl, alkoxy, acyloxy, alkylcarbonyl, alkoxycarbonyl, or NR'_2 where

R' = hydrogen, alkyl or aryl,

Y = a substituent, which contains a substituted or unsubstituted 1,4,6-trioxaspiro-[4,4]-nonane radical,

n = 1, 2 or 3, m = 1, 2 or 3, where $n+m \leq 4$,

and/or from silanes of the general formula (II),



in which the radicals A, R, R_2 and X are the same or different and have the following meaning:

A = O, S, PR', POR', NHC(O)O or NHC(O)NR', where R' = hydrogen, alkyl or aryl,

B = straight-chain or branched organic radical, which is derived from a compound B' having at least one (for l = 1 and A = NHC(O)O or NHC(O)NR') or at least two C=C double bonds and 5 to 50 carbon atoms, where R' = hydrogen, alkyl or aryl,

R = alkyl, alkenyl, aryl, alkylaryl or arylalkyl,

R^2 = alkylene, arylene or alkylene-arylene,

X = hydrogen, halogen, hydroxyl, alkoxy, acyloxy, alkylcarbonyl, alkoxycarbonyl or NR'_2 , where

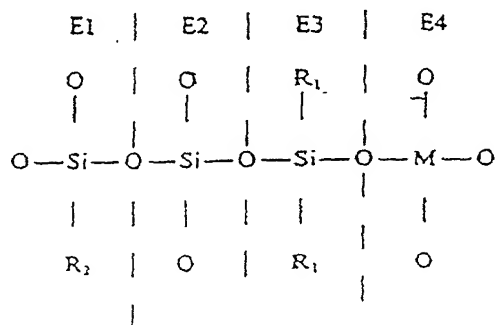
$R' =$ hydrogen, alkyl or aryl,

$n = 1, 2$, or 3 , $k = 0, 1$ or 2 , $l = 0$ or 1 ,

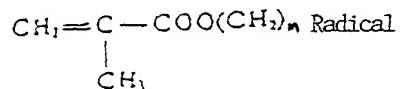
$x =$ a whole number, the maximum value of which corresponds to the number of double bonds in the compound B' minus 1, or is equal to the number of double bonds in the compound B' , when $l = 1$ and A represents $NHC(O)$ or $NHC(O)NR'$,

optionally containing fillers and/or copolymerisable monomers.

In a further example, a compound composed of the structural element E 2 and at least one of the structural elements E 1 and/or E 3 and/or E 4 of the general formula



wherein R_1 denotes a methyl, ethyl, n-propyl, isopropyl or an optionally $CH_3-C_3H_7$ -substituted phenyl radical, R_2 denotes a $CH_2=CH$, $CH_2=CHCOO(CH_2)_n$ or



or R1, n denotes 0, 1, 2 or 3, and M denotes titanium or zirconium, is present in the resin composition. The molar ratio of the structural element E 2 to the structural elements E 1 and/or E 3 and/or E 4 thus lies in each case between 50:1 and 10:1 or the molar ratio of the structural elements E2:E1:E3:E4 lies at about 25:1:1:1. Polymerisation of the polysiloxanes takes place by free radical and/or cationically.

As constituent (b) of the composition, in the case of the free-radical hardening, one or more of the following compounds initiating polymerisation is or are provided: phosphine oxides, acylphosphine oxides, diphenyl-2,4,6-trimethylbenzoylphosphine oxide; benzoin ethers, such as benzoin or the benzoin-alkyl ethers; benzil ketals, such as benzil dialkyl ketal; α -hydroxyketones; α -aminoketones; acetophenones, such as α -hydroxyacetophenones, dialkoxyacetophenones, α -aminoacetophenones, benzophenones; thioxanthenes, such as i-propyl thioxanthone; α -dicarbonyl compounds, such as camphor-quinone; bisimidazoles; metallocenes, such as titanocenes and ferrocenes; aryl-tert.-butyl peresters; xanthenes; fluorenes; and/or fluorones, such as 5,7-diiodo-3-butoxy-6-fluorones.

In the case of cationic hardening, constituent (b) of the composition contains as initiator one or more of the following compounds: aryl diazonium salts, aryl sulphonium salts, aryl iodonium salts, ferrocenium salts and/or phenylphosphonium-benzophenone salts.

In the case of a dual-hardening compound or compound combination of constituent (a), a combination of one or more of the above-mentioned compounds initiating free-radical polymerisation with one or more of the above-mentioned compounds initiating cationic polymerisation, is provided as constituent (b). Hence, the dual-hardening composition and/or required properties may be adjusted.

Constituent (c) may contain as co-initiators for free-radical hardening, one or more of the following compounds: tertiary amines, preferably N,N-dimethyl-p-toluidine, N,N-

dihydroxyethyl-p-toluidine, N,N-dialkyl-dialkylaniline and other structure-related amines, preferably in combination with initiators, such as benzophenones and α -dicarbonyl compounds, such as camphor-quinone; diaryl iodonium compounds, preferably in combination with the fluorone initiators; borates, such as for example butyrylcholine-triphenylbutyl borate and other structure-related borates; organic phosphites; thioxanthenes as sensitisers for the α -aminoacetophenone initiators.

As co-initiators of constituent (c), one or more of the following compounds may be provided for cationic hardening: xanthenes; fluorenes; fluorones; α -dicarbonyl compounds, such as for example camphor-quinone as sensitiser for the diaryl iodonium initiators.

In the case of a dual-hardening composition, a combination of one or more of the above-mentioned co-initiators for free-radical polymerisation with one or more of the above-mentioned co-initiators for cationic polymerisation, such as for example a combination of fluorones, diaryl iodonium salts, tertiary amines and/or borates, may be provided together with corresponding initiators of constituent (b) as constituent (c).

Constituent (d) may contain at least one modifier, for example contain at least one pigment and/or a dyestuff, such as for example anthraquinone, preferably in a quantity of 0-3 wt.%. The dyestuff/ pigment is precisely matched to the light source used, or its emission spectrum. This means, if a different light source is used, if possible the dyestuff/pigment must also be changed.

At least one of the following materials may be provided as suitable filler of constituent (d) of the composition: silicon dioxide, such as pyrogenic silicon dioxide and/or amorphous silicic acid, aluminium oxide, ceramic, quartz, ground glasses, fragment polymers, silica gels and minerals. To improve bonding with the remaining constituents of the composition, the filler may be pretreated with a silane, such as for example 3-

methacryloyloxypropyl trimethoxysilane. The grain sizes of the inorganic fillers are conventionally 0.01-100 μm , preferably 0.01-20 μm .

Furthermore, fibres and fabrics, such as for example glass fibres, carbon fibres, textile fibres, metal fibres, may be embedded as fillers. This includes fibres and fabrics individually or in tape, mat, hose or cord form or a bundle of continuous fibres. It is thus not important whether the filler is present in the plastic from the start or whether the polymerisation process is interrupted, in order to insert, for example a glass-fibre mat. If the plastic formulation contains the filler, a liquid, semi-solid to solid paste is obtained regardless of the filler content. Semi-solid or solid pastes are brought to the defined layer thickness (for example 10 – 150 μm), deviating from Figure 1, by a roller system. The introduction of fillers makes possible a plurality of further areas of use, such as for example dental and otoplastics applications and applications in face and bone surgery.

In addition, constituent (d) of the composition may contain stabilisers, such as hydroquinone, hydroquinone monomethyl ether, pyrocatechol and/or 2,6-di-tert.-butyl-4-methylphenol, preferably in a quantity of 0-5 wt.%.

Examples of a composition of the invention are mentioned in the following table.

Constituent	Designation	Example 1 Wt.%	Example 2 Wt.%	Example 3 Wt.%	Preferred Range Wt.%
(a)	1,4-Butane diol dimethacrylate	29.0	13	29.5	20 – 40
(a)	Aliphatic diurethane methacrylate	35.1	20	35	10 – 50
(a)	Tetra- ethoxylated bisphenol A dimethacrylate	-	37.7	-	15 – 45
(a)	Aliphatic urethane methacrylate	30.0	25	30	15 – 45
(d)	Anthraquinone dyestuff	1.0	0.3	0.6	0.1 – 1.5
(c)	Tertiary amine	2.0	2.0	2.0	0.3 – 4
(b)	Acylphosphine oxide	1.0	0.1	1.0	0.05 – 1.0
(b)	Fluorone initiator	0.5	0.5	0.5	0.05 – 1.5
(c)	Iodonium salt	1.4	1.4	1.4	0.1 – 5

When using the composition indicated in Example 1 as the plastic 6 in the process described above, curing depths of 115-211 μm may be obtained for illumination times of 4-12 seconds. Hence, layer thicknesses of 55 – 105 μm are produced with the above-mentioned arrangement. Layer thicknesses of 1 – 250 μm are achieved by varying the plastic composition. A halogen lamp is used in the process.

The composition is produced by the following essential steps: initially prescribed quantities of initiators, co-initiators, dyestuffs, pigments and stabilisers are dissolved in a slightly viscous part of constituent (a) of the composition, such as for example in the

monomer ethyl methacrylate or butane diol dimethacrylate, wherein the resulting mixture are stirred depending on solubility capacity of the constituents used for between 1-36 hours at 20-80°C. The resulting solution is then mixed with the rest of constituent (a) of the composition for 10-60 minutes. Optionally one or more fillers are then added to the resulting solution in small portions and mixed intensively after every addition.

During production, physical properties, such as the hardness or depth of hardness of a layer, the modulus of elasticity, the colour, the layer thickness and the durability of the object to be formed may be influenced by the selection of type and quantity of the fillers, pigments, dyestuffs and stabilisers of the composition and adjusted as required. Furthermore, the initiators and/or co-initiators may be used in different combinations in order to vary them according to the type of shaping process, the light source thus used and the required physical properties of the object to be formed therewith.

In the case of a dual-hardening composition, the accuracy of fit of the object to be formed may be improved, since, for example compared to a composition hardening purely by free radical, the polymerisation shrinkage and the interfering influence of an oxygen inhibition layer is reduced.

By precise matching of the composition of the plastic used in the shaping process, the light source used, the mask, the type and/or the intensity of the radiated light, the thickness of a layer to be hardened in the shaping process may be adjusted to the required thickness. In addition, the layer thickness and the depth of hardness over the polymerisation depth and the polymerisation time may be influenced by adding suitable dyestuffs and/or by varying the concentrations of the initiators and/or co-initiators or by the selection and combination of one or more initiators and/or one or more co-initiators.

The plastic of the above-mentioned composition may be used in the process described above for forming a three-dimensional object, that is during microphotosolidification, and

also for other rapid-prototyping processes, for example during laser sintering or in stereolithography.

The use of the composition of the invention is not restricted to microphotosolidification or to rapid-prototyping processes. The composition of the invention can rather also be used for other shaping processes, such as for example during film-casting of plastics, in the production of plastic sintered parts or in microstructuring, such as for example during photolithography in semi-conductor technology. In addition, the composition of the invention can be used in the dental field, the field of face and bone surgery and the otoplastic field for producing inlays, onlays, tooth fillings, attachments, crowns, bridges, artificial teeth, crown teeth, tooth prostheses, tooth implants, face implants, bone implants and hearing aids (otoplastics). Consequently, both models and also individually made single products or mass-produced sales products may be produced using the composition of the invention.

A specific use of the composition of the invention is given in dental technology in a process for producing plastic inlays. In the process, initially an image of a cavity of a tooth to be filled is made in known manner using a camera and a computer model of the inlay to be inserted in the cavity is produced. The computer model is then divided into flat layers by means of software, wherein the layer data thus produced supplies the control of a microphotosolidification plant described above, where the inlay is built up layer by layer corresponding to the layer data. Inlays can thus be produced in precise manner by good resolution during the process of microphotosolidification. In the process of the invention, a plastic as described above is used, which is tooth-coloured by addition of appropriate dyestuffs/pigments.

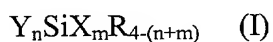
Alternatively, the inlay may also be produced by using a plastic which is paste-like due to a filler of constituent (d), wherein each layer is produced by rolling-out the paste-like material. Particular stiffness of the inlay produced can be achieved if glass-fibre

constituents are added to the plastic composition to be cured. Alternatively, after curing one or more plastic layers, a glass-fibre mat may also be laid therebetween.

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PATENT CLAIMS

1. Composition which cures using visible light containing
 - (a) 2-99 wt.% of at least one compound which contains at least one acrylate group and/or at least one methacrylate group and/or at least one vinyl group and/or at least one epoxy group and/or at least one oxetane group and/or at least one acryl-epoxy oligomer group and/or at least one methacryl-epoxy oligomer group, and/or at least one resin composition based on at least one polymerisable polysiloxane,
 - (b) 0.01-7 wt.% of at least one initiator,
 - (c) 0-5 wt.% of at least one co-initiator,
 - (d) 0-85 wt.% of one or more modifiers, such as fillers, dyestuffs, pigments, flow improvers, thixotropic agents, polymeric thickeners, oxidising additives, stabilisers and retardants.
2. Composition according to claim 1, characterised in that at least one ormocer is present in the resin composition as polymerisable polysiloxane.
3. Composition according to claim 1 or 2, characterised in that as resin composition, a resin composition based on polymerisable polysiloxanes which can be hardened photochemically or thermally in the presence of initiators or one which is self-hardening, which can be obtained by hydrolytic condensation of one or more hydrolytically condensable compounds of silicon and optionally other elements from the group B, Ba, Ti, Zr, Al, Sn, the transition metals, the lanthanides and the actinides, and/or pre-condensates derived from the above-mentioned compounds, optionally in the presence of a catalyst and/or a solvent, by the action of water or moisture, wherein 1 to 100 mole %, based on the monomeric compounds, are selected from silanes of the general formula (I),



in which the radicals X, Y and R are the same or different and have the following meaning:

R = alkyl, alkenyl, aryl, alkylaryl or arylalkyl

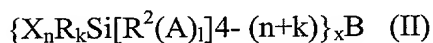
X = hydrogen, halogen, hydroxyl, alkoxy, acyloxy, alkylcarbonyl, alkoxy carbonyl, or NR'_2 where

R' = hydrogen, alkyl or aryl,

Y = a substituent, which contains a substituted or unsubstituted 1,4,6-trioxyaspiro-[4,4]-nonane radical,

n = 1, 2 or 3, m = 1, 2 or 3, where $n+m \leq 4$,

and/or from silanes of the general formula (II),



in which the radicals A, R, R_2 and x are the same or different and have the following meaning:

A = O, S, PR', POR', $\text{NHC}(\text{O})\text{O}$ or $\text{NHC}(\text{O})\text{NR}'$, where R' = hydrogen, alkyl or aryl,

B = straight-chain or branched organic radical, which is derived from a compound B' having at least one (for l = 1 and A = $\text{NHC}(\text{O})\text{O}$ or $\text{NHC}(\text{O})\text{NR}'$) or at least two C=C double bonds and 5 to 50 carbon atoms, where R' = hydrogen, alkyl or aryl,

R = alkyl, alkenyl, aryl, alkylaryl or arylalkyl,

R^2 = alkylene, arylene or alkylene-arylene,

X = hydrogen, halogen, hydroxyl, alkoxy, acyloxy, alkylcarbonyl, alkoxy carbonyl or NR'_2 , where

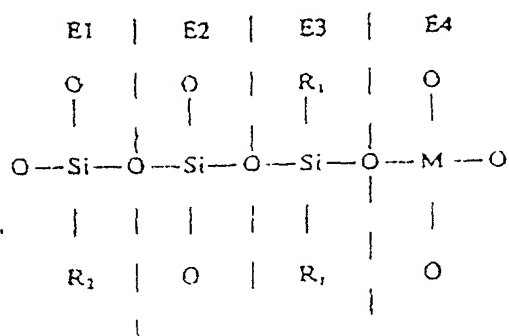
R' = hydrogen, alkyl or aryl,

n = 1, 2, or 3, k = 0, 1 or 2, l = 0 or 1,

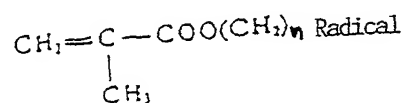
x = a whole number, the maximum value of which corresponds to the number of double bonds in the compound B' minus 1, or is equal to the number of double bonds in the compound B', when l = 1 and A represents $\text{NHC}(\text{O})$ or $\text{NHC}(\text{O})\text{NR}'$,

optionally containing fillers and/or copolymerisable monomers.

4. Composition according to one of claims 1 to 3, characterised in that a compound composed of the structural element E 2 and at least one of the structural elements E 1 and/or E 3 and/or E 4 of the general formula



wherein R₁ denotes a methyl, ethyl, n-propyl, isopropyl or an optionally CH₃-C₃H₇-substituted phenyl radical, R₂ denotes a CH₂=CH, CH₂=CHCOO(CH₂)_n or



or R₁, n denotes 0, 1, 2 or 3, and M denotes titanium or zirconium, is present in the resin composition.

5. Composition according to one of claims 1 to 4, characterised in that it contains the compound of constituent (a) in a quantity of 10-95 wt.%.
6. Composition according to one of claims 1 to 5, characterised in that the composition can be cured in a wavelength range from 350-700 nm.
7. Composition according to one of claims 1 to 6, characterised in that constituent (a) contains aliphatic diurethane methacrylate, tetra-ethoxylated bisphenol A dimethacrylate, aliphatic urethane methacrylate, 2-hydroxyethyl acrylate, hydroxypropyl acrylate, methyl methacrylate, ethyl methacrylate, n-propyl methacrylate, iso-propyl methacrylate, butyl methacrylate, 2-ethylhexyl methacrylate, methacrylic acid esters, isobornyl methacrylate, benzyl methacrylate, cyclohexyl methacrylate, n-hexyl methacrylate, ethyl triglycol methacrylate, tetrahydrofurfuryl methacrylate, hydroxyalkyl methacrylates, 2-hydroxyethyl methacrylate, alkoxyethyl methacrylate, allyl methacrylate, ethylene glycol dimethacrylate, diethyl glycol dimethacrylate, triethylene glycol dimethacrylate, tetraethylene glycol dimethacrylate, polyethylene glycol dimethacrylates, 1,3-butane diol dimethacrylate, 1,4-butane diol dimethacrylate, 1,6-hexane diol dimethacrylate, 1,12-dodecane diol dimethacrylate, glycerin-1,3-dimethacrylate, diurethane dimethacrylate, trimethylol propane trimethylacrylate, 1,3,5,7-tetrakis-(2,1-ethanediyl-3,4-epoxycyclohexyl)-1,3,5,7-tetramethylcyclotetrasiloxane, 1,10-decanediyl-bis(oxymethylene)bis(3-ethyloxetane), 1,3,5,7,9-pentakis(2,1-ethanediyl-3,4-epoxycyclohexyl)-1,3,5,7,9-pentamethylcyclopentasiloxane, vinylcyclohexene oxide, vinylcyclohexene dioxide, 3,4-epoxy-6-methylcyclohexylmethyl-3,4-epoxy-6-methylcyclohexane carboxylate, bis(2,3-epoxycyclopentyl)ether; 3,4-epoxy-6-methylcyclohexylmethyl adipate, 3,4-epoxycyclohexyl-5,5-spiro-3,4-epoxy(cyclohexane-metadioxane), 1,4-butanediyl-bis(oxymethylene)bis(3-ethyloxetane), 3,4-epoxycyclohexylmethyl-3,4-epoxycyclohexane carboxylate, 1,1,3,3-tetramethyl-1,3-bis(2,1-ethanediyl-3,4-epoxycyclohexyl)disiloxane, bis-(3,4-epoxycyclohexylmethyl) adipate, monovinyl ether, divinyl ether, hydroxyvinyl ether, aminovinyl ether, trivinyl

ether, triethylene glycol divinyl ether, 4-hydroxybutylvinyl ether, propenyl ether from propylene carbonate, dodecyl-vinyl ether, triethylene glycol divinyl ether, alkyl-vinyl ether, ethylene glycol-monovinyl ether, diethylene glycol divinyl ether, butane diol-monovinyl ether, butane diol-divinyl ether, hexane diol-divinyl ether, ethylene glycol-butyl-vinyl ether, cyclohexane-dimethanol-monovinyl ether and cyclohexane-dimethanol-divinyl ether, 2-ethyl-hexyl-vinyl ether, poly-THF-divinyl ether, cyclohexyl-vinyl ether, tert.-butyl-vinyl ether, tert.-amyl-vinyl ether, ethylene glycol-divinyl ether, diethylene glycol-monovinyl ether, hexane diol-monovinyl ether, tetraethylene glycol-divinyl ether, trimethylol-propane-trivinyl ether, aminopropylvinyl ether and/or 2-diethylaminoethyl-vinyl ether.

8. Composition according to one of claims 1 to 7, characterised in that constituent (b) contains for free-radical hardening, phosphine oxides, benzoin ethers, benzil ketals, acetophenones, benzophenones, thioxanthenes, α -dicarbonyl compounds, bisimidazoles, metallocenes, aryl-tert.-butyl peresters and/or fluorones, for cationic hardening, aryl diazonium salts, aryl sulphonium salts, aryl iodonium salts, ferrocenium salts and/or phenylphosphonium-benzophenone salts or a mixture thereof.

9. Composition according to claim 8, characterised in that as phosphine oxide, diphenyl-2,4,6-trimethylbenzoylphosphine oxide, as benzoin ether, benzoin and/or benzoin-alkyl ether, as benzil ketals, benzil dialkyl ketals, as acetophenones, α -hydroxyacetophenones, dialkoxyacetophenones and/or α -aminoacetophenones, as thioxanthone, i-propylthioxanthone, as α -dicarbonyl compound, camphor-quinone, as metallocenes, titanocenes and/or ferrocenes, as fluorones, 5,7-diiodo-3-butoxy-6-fluorones, are present.

10. Composition according to one of claims 1 to 9, characterised in that constituent (c) contains for free-radical hardening, tertiary amines, diaryl iodonium compounds, borates, organic phosphites and/or thioxanthenes,

for cationic hardening, xanthenes, fluorenes, fluorones and/or α -dicarbonyl compound, or a mixture thereof.

11. Composition according to claim 10, characterised in that as tertiary amine, N,N-dimethyl-p-toluidine, N,N-dihydroxyethyl-p-toluidine, N,N-dialkyl-alkylaniline and/or other structure-related amines, as borates, butyrylcholine-triphenylbutyl borate and/or other structure-related borates, are present.

12. Composition according to one of claims 1 to 11, characterised in that constituent (d) contains an anthraquinone dyestuff.

13. Composition according to one of claims 1 to 12, characterised in that constituent (d) contains as filler, silicon dioxide, pyrogenic silicon dioxide, amorphous silicic acid, aluminium oxide, ceramic, quartz, ground glass, fragment polymer, silica gel, minerals, fibres and/or fabrics.

14. Composition according to claim 13, characterised in that as fibres and/or fabrics, glass fibres, carbon fibres, textile fibres and/or metal fibres, are present individually or in tape, mat, hose or cord form or in the form of a bundle of continuous fibres.

15. Composition according to claim 14, characterised in that one or more of the fillers present are silanised.

16. Composition according to one of claims 1 to 15, characterised in that constituent (d) contains hydroquinone, hydroquinone monomethyl ether, pyrocatechol, 2,6-di-tert.-butyl-4-methylphenol.

17. Use of a composition according to one of claims 1 to 16 in a shaping process.

18. Use of a composition according to one of claims 1 to 16 for producing models, individually manufactured single products and mass-produced sales products.

19. Use of a composition according to one of claims 1 to 16 in a process of microsolidification, rapid-prototyping, film casting, the production of plastic sintered parts, microstructuring, photolithography, the production of dental products, the production of surgical implants and/or the production of otoplastic products.

20. Use of a composition according to one of claims 1 to 16 in a process for producing a three-dimensional object by sequential selective solidification of layers of the composition at positions corresponding to the cross-section of the object under the action of visible light.

21. Process for producing a tooth filling by sequential layered solidification of a composition according to one of claims 1 to 13 at positions corresponding to the cross-section of the filling in the particular layer.

22. Process according to claim 21, characterised by the steps

- a) producing a computer model of the filling to be produced,
- b) dividing the computer model into layers, which correspond in each case to a cross-section of the filling,
- c) layered curing of the composition at positions corresponding to the cross-section of the filling under the action of visible light.

23. Process according to claim 21 or 22, characterised in that a paste-like composition is used.

24. Process according to claim 23, characterised in that glass-fibre constituents are admixed to the composition.

25. Object which is produced by curing the composition according to one of claims 1 to 13 by means of visible light.

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ABSTRACT

A composition which cures using visible light is indicated, having

- (a) 2-99 wt.% of at least one compound which contains acrylate and/or methacrylate groups, and/or vinyl and/or epoxy and/or oxetane groups and/or acryl-epoxy oligomer groups and/or methacryl-epoxy oligomer groups, and/or at least one resin composition based on polymerisable polysiloxanes,
- (b) 0.01-7 wt.% of at least one initiator,
- (c) 0-5 wt.% of at least one co-initiator,
- (d) 0-85 wt.% of one or more modifiers, such as fillers, dyestuffs, pigments, flow improvers, thixotropic agents, polymeric thickeners, oxidising additives, stabilisers and retardants.

(Figure 1)

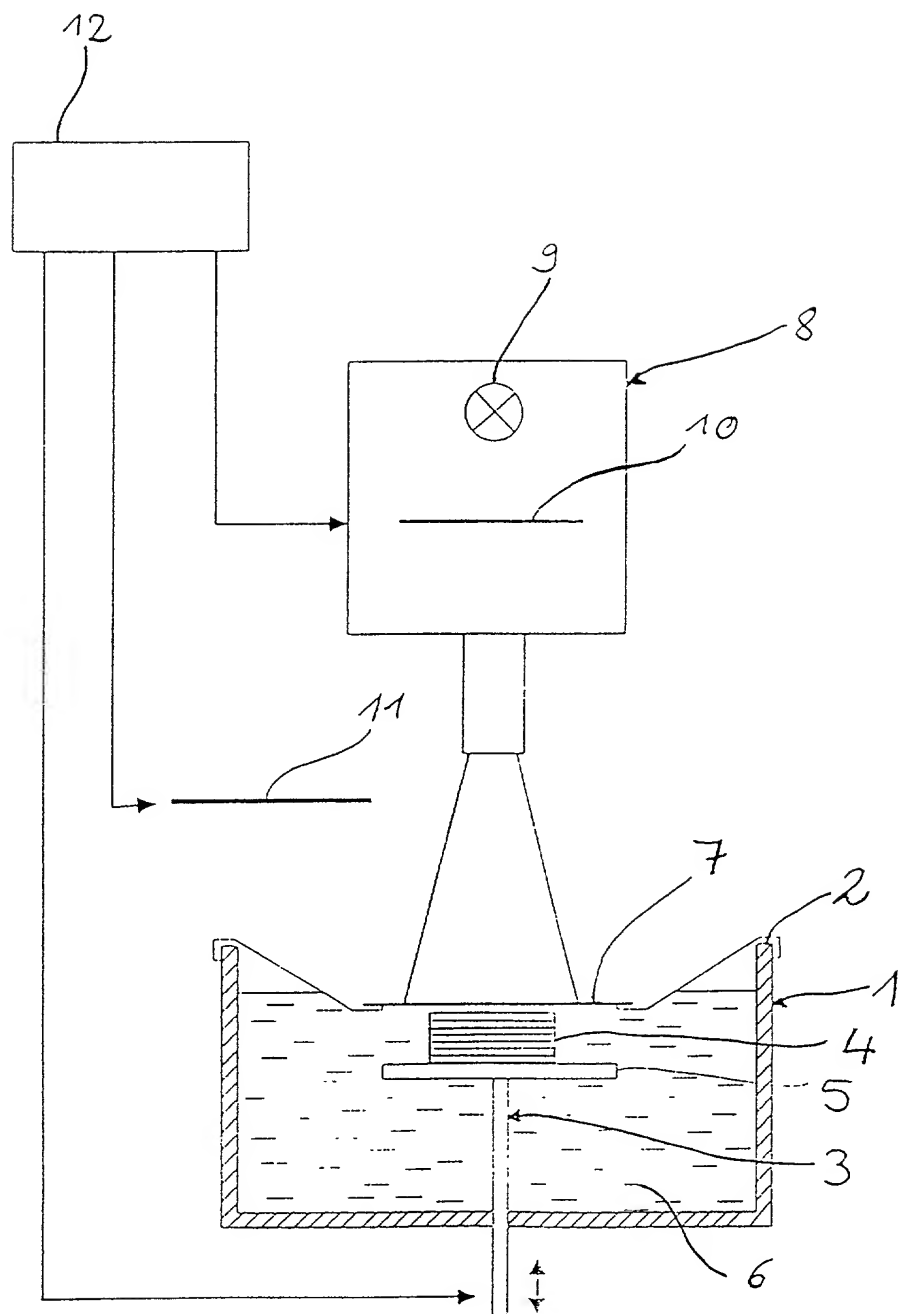


Fig. 1

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DECLARATION AND POWER OF ATTORNEY

As a below named inventor, I hereby declare that: My residence, post office address and citizenship are as stated below next to my name. I believe I am the original, first and sole inventor (if only one name is listed at 201) below or an original, first and joint inventor (if plural names are listed at 201-206 below) of the subject matter which is claimed and for which a patent is sought on the invention entitled: COMPOSITION WHICH CURES USING VISIBLE LIGHT AND ITS USE

which is described and claimed in:

- ☒ the specification attached hereto.
- ☐ the specification in U.S. Application Serial Number _____, filed on _____.
- ☐ the specification in PCT international application Number, _____, filed on _____; and was amended on _____.

I hereby state that I have reviewed and understand the contents of the above identified specification, including the claims, as amended by any amendment referred to above. I acknowledge the duty to disclose information which is material to the examination of this application in accordance with Title 37, Code of Federal Regulations, §1.56(a). I hereby claim foreign priority benefits under Title 35, United States Code, §119 of any foreign application(s) for patent or inventor's certificate listed below and have also identified below any foreign application for patent or inventor's certificate having a filing date before that of the application on which priority is claimed.

Prior Foreign/PCT Applications and Any Priority Claims Under 35 U.S.C. §119:			
Application No.	Filing Date	Country	Priority Claimed Under 35 U.S.C. §119?
199 38 463.0	August 13, 1999	Germany	<input checked="" type="checkbox"/> YES <input checked="" type="checkbox"/> NO
199 50 284.6	October 19, 1999	Germany	<input checked="" type="checkbox"/> YES <input checked="" type="checkbox"/> NO
			<input type="checkbox"/> YES <input type="checkbox"/> NO

I hereby claim the benefit under 35 U.S.C. §120 of any United States application(s) or PCT international application(s) designating the United States of America that is/are listed below, and, insofar as the subject matter of each of the claims of this application is not disclosed in that/those prior application(s) in the manner provided by the first paragraph of 35 U.S.C. §112, I acknowledge the duty to disclose material information as defined in 37 CFR §1.56(a) which occurred between the filing date of the prior application(s) and the national or PCT international filing date of this application:

Prior U.S. Applications or PCT International Applications Designating the U.S-Benefit Under 35 U.S.C. §120				
U.S. Applications		Status (Check One)		
Application Serial No.	U.S. Filing Date	Patented	Pending	Abandoned
PCT Applications Designating the U.S.				
Application No.	Filing Date	U.S. Serial No. Assigned		
PCT/EP00/07317	July 28, 2000			

**CLAIM FOR BENEFIT OF PRIOR U.S. PROVISIONAL APPLICATION(S)
(35 U.S.C. §119(e))**

I hereby claim the benefit under Title 35, United States Code, §119(e) of any United States provisional application(s) listed below:

Applicant	Provisional Application Number	Filing Date

POWER OF ATTORNEY: As a named inventor, I hereby appoint the following attorney(s) with full powers of association, substitution and revocation to prosecute this application and transact all business in the Patent and Trademark Office connected therewith.

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	POST OFFICE ADDRESS	POST OFFICE ADDRESS	CITY	STATE OR COUNTRY AND ZIP CODE
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	POST OFFICE ADDRESS	POST OFFICE ADDRESS	CITY	STATE OR COUNTRY AND ZIP CODE

I hereby further declare that all statements made herein of my own knowledge are true and that all statements made on information and belief are believed to be true; and further, that these statements were made with the knowledge that willful false statements and the like so made are punishable by fine or imprisonment, or both, under Section 1001 of Title 18 of the United States Code, and that such willful false statements may jeopardize the validity of the application or any patent issued thereon.

Signature of Inventor 201 <i>Michael J. J. J.</i>	Signature of Inventor 202 <i>Ridgely J. J.</i>
Date: <i>8. Jan. 2002</i>	Date: <i>8. Jan. 2002</i>
Signature of Inventor 203	Signature of Inventor 204
Date:	Date:
Signature of Inventor 205	Signature of Inventor 206
Date:	Date:

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